

Ionic liquids

The present invention relates to novel ionic liquids with the general formula [cation] [R'-SO₄], wherein R' is a branched or linear, saturated or unsaturated, 5 aliphatic or alicyclic, functionalized or non-functionalized hydrocarbon chain with 3 - 36 carbon atoms. These novel ionic liquids can be used e.g. as solvents or solvent additives in chemical reactions, as extraction agents or as heat carriers.

Technical context of the invention

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The term ionic liquids should be understood to mean salts or mixtures of salts whose melting point is below 100 °C (P. Wasserscheid, W. Keim, *Angew. Chem.*, **2001**, 112, 3926). Salts of this type known from the literature consist of anions, such as halogenostannates, halogenoaluminates, hexafluorophosphates or 15 tetrafluoroborates combined with substituted ammonium cations, phosphonium cations, pyridinium cations or imidazolium cations. Several publications have already described the use of ionic liquids as solvents for chemical reactions (T. Welton, *Chem. Rev.* **1999**, 99, 2071, P. Wasserscheid, W. Keim, *Angew. Chem.*, **2000**, 112, 3926). For example, hydrogenation reactions of olefins with 20 rhodium(I) (P. A. Z. Suarez, J. E. L. Dullius, S. Einloft, R. F. de Souza and J. Dupont, *Polyhedron* 15/7, **1996**, 1217-1219), ruthenium(II) and cobalt(II) complexes (P. A. Z. Suarez, J. E. L. Dullius, S. Einloft, R. F. de Souza and J. Dupont, *Inorganica Chimica Acta* 255, **1997**, 207-209) have been carried out successfully in ionic liquids with tetrafluoroborate anion. The hydroformylation of 25 functionalized and non-functionalized olefins is possible with rhodium catalysts in ionic liquids with weakly coordinating anions (e.g. PF₆⁻, BF₄⁻) (Y. Chauvin, L. Mussmann, H. Olivier, *European Patent*, EP 776880, **1997**; Y. Chauvin, L. Mussmann, H. Olivier, *Angew. Chem., Int. Ed. Engl.*, **1995**, 34, 2698; W. Keim, D. Vogt, H. Waffenschmidt, P. Wasserscheid, *J. of Cat.*, **1999**, 186, 481).

30 Further important fields of application of ionic liquids consists of their use as extraction agents for material separation (J. G. Huddleston, H. D. Willauer, R. P. Swallows, A. E. Visser, R. D. Rogers, *Chem. Commun.* **1998**, 1765-1766; b) A. E. Visser, R. P. Swatlowski, R. D. Rogers, *Green Chemistry* **2000**, 2(1), 1-4) and of their use as heat carrier (M. L. Mutch, J. S. Wilkes, *Proceedings of the 35 Eleventh International Symposium on Molten Salts*, P. C. Trulove, H. C. De Long,

G. R. Stafford and S. Deki (Editors), Proceedings Volume 98-11, The Electrochemical Society, Inc, Pennington, NJ; 1998, page 254).

Background and formulation of the problem involved

5 Even if the definition of an ionic liquid includes those salts whose melting point is between the room temperature and 100 °C it is still necessary and desirable for many applications for the ionic liquids to be liquid at temperatures below room temperature.

Numerous examples of such ionic liquids are known; however, as a rule these 10 systems possess halide ions such as F⁻, Cl⁻, Br⁻ or I⁻ or those anions which contain halogen atoms. Typical representatives of the latter anions are - without any claim to completeness - [BF₄]⁻, [PF₆]⁻, [CF₃COO]⁻, [CF₃SO₃]⁻, [(CF₃SO₂)₂N]⁻, [AlCl₄]⁻, [Al₂Cl₇]⁻ or [SnCl₃]⁻. The use of such anions containing halogen atoms imposes serious restrictions on the applicability of the corresponding ionic 15 liquids: a) The use of these anions leads to considerable costs since even the alkali salts of these ions are very expensive; b) The hydrolysis products of these anions containing halogen atoms lead to considerable corrosion in steel reactors and in some instances also in glass reactors; c) The thermal disposal of a "spent" ionic liquid with anions containing halogen atoms usually causes corrosion and 20 environmental problems and is therefore very costly. The disposal via degradation in a biological clarification plant is also rendered difficult by the presence of anions containing halogen atoms.

In general, those ionic liquids free from halogen atoms are therefore of particular interest which combine the following five properties:

25 a) a melting point and/or glass transition point of less than 25 °C;
b) hydrolysis-stable in neutral aqueous solution (pH = 7) up to 80 °C;
c) to be disposed of by thermal means without the formation of problematic combustion gases
d) degradable in biological clarification plants
30 e) The anion is commercially available as alkali salt at a favorable price.

Among the ionic liquids free from halogen atoms according to the state of the art, there have been no representatives so far capable of satisfying this complex technical requirement profile. Thus nitrate melts, nitrite melts, sulfate melts (J.

S. Wilkes, M. J. Zaworotko, *J. Chem. Soc. Chem. Commun.* **1992**, 965) and benzene sulfonate melts (H. Waffenschmidt, Dissertation, RWTH Aachen 2000) are known, however, these ionic liquids have melting points above room temperature. Hydrogen sulfates and hydrogen phosphates react in aqueous 5 solution while splitting off one or several protons and form acidic aqueous solutions. Methyl sulfate and ethyl sulfate melts exhibit a distinct hydrolysis after only 1 h at 80 °C in aqueous solution with the formation of hydrogen sulfate anions and the corresponding alcohol (compare also comparative examples 1 and 2).

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Our invention as a solution to the problem

Our invention is based on the surprising finding that ionic liquids consisting of a combination of a suitable organic cation – with imidazolium cations, pyridinium cations, phosphonium cations or ammonium cations being particularly suitable 15 examples – with anions with the general formula $[R-SO_4]$ – R being a linear or branched, saturated or unsaturated, aliphatic or alicyclic, functionalized or non-functionalized alkyl radical with 3 - 36 carbon atoms – are characterized precisely by the above-mentioned, highly interesting and technically relevant combination of properties: The novel ionic liquids according to the invention possess, on the 20 one hand, a melting point and/or glass transition point of less than 25 °C, they are, moreover, hydrolysis-stable in neutral aqueous solution (pH = 7) up to 80 °C. Moreover, the ionic liquids according to this invention cause no problems during thermal disposal since only CO₂, H₂O and SO₂ are formed during their combustions. A further essential advantage of the novel ionic liquids according to 25 the invention is the fact that many alkali salts with the general formula [alkalinization] $[R-SO_4]$ – in which R is a linear or branched, functionalized or non-functionalized, saturated or unsaturated, aliphatic or alicyclic alkyl radical with 3 - 36 carbon atoms – are raw materials readily available in industry for detergents and for products in the cosmetics and cleaning agents sector. This 30 has lead to an extraordinarily high level of knowledge on the toxicological properties and the biological degradation behavior of the anion component $[RSO_4]$. From this, the conclusion can be drawn that the disposal of the ionic liquids according to the invention "spent" in technical applications can be carried out without problems in biological clarification plants.

35 The combination of these five properties, which, technically speaking, is highly

interesting, characterizes the novel ionic liquids according to this invention as ideal solvents and/or solvent additives for stoichiometric or catalytic chemical reactions and for their use as extraction agents and as heat carriers.

Particularly preferably those ionic liquids, too, can be produced and used according to the invention which contain mixtures of different anions with the general formula $[RSO_4]$ - R being a linear or branched, saturated or unsaturated, aliphatic or alicyclic, functionalized or non-functionalized alkyl radical with 3 - 36 carbon atoms. These systems can be easily obtained from the mixtures of the corresponding alkali salts which are available in industry.

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In detail, the following novel ionic liquids according to the invention and their mixtures deserve to be mentioned:

1-ethyl-3-methylimidazolium butyl sulfate

15 1-ethyl-3-methylimidazolium octyl sulfate

1-ethyl-3-methylimidazolium 2-ethylhexyl sulfate

1-ethyl-3-methylimidazolium dodecyl sulfate

1-butyl-3-methylimidazolium butyl sulfate

1-butyl-3-methylimidazolium octyl sulfate

20 1-butyl-3-methylimidazolium 2-ethylhexyl sulfate

1-butyl-3-methylimidazolium dodecyl sulfate

1-hexyl-3-methylimidazolium butyl sulfate

1-hexyl-3-methylimidazolium octyl sulfate

1-hexyl-3-methylimidazolium 2-ethylhexyl sulfate

25 1-hexyl-3-methylimidazolium dodecyl sulfate

1-octyl-3-methylimidazolium butyl sulfate

1-octyl-3-methylimidazolium octyl sulfate

1-octyl-3-methylimidazolium 2-ethylhexyl sulfate

1-octyl-3-methylimidazolium dodecyl sulfate

30 1-decyl-3-methylimidazolium butyl sulfate

1-decyl-3-methylimidazolium octyl sulfate

1-decyl-3-methylimidazolium 2-ethylhexyl sulfate

1-decyl-3-methylimidazolium dodecyl sulfate

1-dodecyl-3-methylimidazolium butyl sulfate

35 1-dodecyl-3-methylimidazolium octyl sulfate

- 1-dodecyl-3-methylimidazolium 2-ethylhexyl sulfate
- 1-dodecyl-3-methylimidazolium dodecyl sulfate
- 1-dodecyl-3-methylimidazolium tetrafluoroborate
- 1-butyl-pyridinium butyl sulfate
- 5 1-butyl-pyridinium octyl sulfate
- 1-butyl-pyridinium 2-ethylhexyl sulfate
- 1-butyl-pyridinium dodecyl sulfate
- trimethyldecylammonium butyl sulfate
- trimethyldecylammonium octyl sulfate
- 10 trimethyldecylammonium 2-ethylhexyl sulfate
- trimethyldecylammonium dodecyl sulfate
- trioctylmethylammonium butyl sulfate
- trioctylmethylammonium octyl sulfate
- trioctylmethylammonium 2-ethylhexyl sulfate
- 15 trioctylmethylammonium dodecyl sulfate
- trimethyldecylammonium butyl sulfate
- trimethyldecylammonium octyl sulfate
- trihexyltetradecylphosphonium butyl sulfate
- trihexyltetradecylphosphonium octyl sulfate
- 20 trihexyltetradecylphosphonium 2-ethylhexyl sulfate
- trihexyltetradecylphosphonium dodecyl sulfate

Examples**Example 1: 1,3-Dimethylimidazoliumoctyl sulfate ([MMIM] [OcSO₄])****Synthesis:**

5 To a solution of 47.18 g (355.8 mmole) of 1,3-dimethylimidazolium chloride ([MMIM] Cl) in 400 ml of methylene chloride rendered absolute, 95.00 g (minimum 355.8 mmole) of sodium octyl sulfate (technical grade; content \geq 87%) are added in small portions. The batch is stirred for 40 hours under blanketing gas. The solid is filtered off and washed with methylene chloride. The
10 organic phase is concentrated and dried under a high vacuum to give 87.55 g [MMIM] [OcSO₄] (285.7 mmole; 80% of the theoretical yield) in the form of a yellowish liquid.

NMR:

15 ¹H-NMR (300 MHz, d⁶-DMSO): δ = 8.87 (s, 1H, N-CH-N), 7.45, 7.44 (one s in each case, 1H in each case, N-CH), 3.87 (mult., 8H, N-CH₃, S-O-CH₂-), 1.57 (mult., 2H, S-O-CH₂-CH₂-), 1.29 (k.B., 10H, S-O-CH₂-CH₂-CH₂-(CH₂)₅-), 0.89 (t, J=6.6 Hz, 3H, -CH₂-CH₃) ppm,
20 ¹³C-NMR (75 MHz, d⁶-DMSO): δ = 136.7, 122.8, 116.8, 35.1, 30.9, 28.7, 28.4, 25.1, 21.7, 12.8 ppm,

Viscosity:

The product exhibits a structural viscosity. The viscosity is strongly dependent on the conditions of measurement.

**Example 2: 1-n-Butyl-3-methylimidazolium octyl sulfate ([BMIM]
[OcSO₄])**

Preparation:

5 84.55 g (0.484 mole) of 1-butyl-3-methylimidazolium chloride (BMIM Cl) and 101.1 g (minimum 0.379 mole) of sodium octyl sulfate (technical grade; content \geq 87%) are dissolved in 200 ml of hot water. The water is slowly removed under vacuum. The solid formed is filtered off after dissolving the batch in methylene chloride. The filtrate is washed until the aqueous phase is colorless and free from 10 chloride. The organic phase is dried over Na₂SO₄. Concentrating and drying under a high vacuum gives 111.0 g (0.319 mmole; 73% of the theoretical yield, based on sodium octyl sulfate) of an oily yellow liquid.

NMR

15 ¹H-NMR (300 MHz, d⁶-DMSO): δ = 9.16 (s, 1H, N-CH-N), 7.80, 7.72 (s in each case, 1H in each case, N-CH), 4.18 (t, 3J=7.1 Hz, 2H, N-CH₂-), 3.86 (s, 3H, N-CH₃), 3.71 (t, 3J=6.6 Hz, 2H, S-O-CH₂), 3.71 (p, 3J=7.3 Hz, 2H, N-CH₂-CH₂-), 1.47 (k.B., 2H, N-CH₂-CH₂-CH₂-), 1.22 (mult., 12H, S-O-CH₂-(CH₂)₆-), 0.81-0.90 (each tr, each 3H, -CH₃) ppm.

20 ¹³C-NMR (75 MHz, d⁶-DMSO): δ = 136.9, 123.9, 122.6, 66.0, 55.2, 48.8, 36.0, 31.8, 31.6, 29.4, 29.1, 25.9, 22.4, 19.1, 14.2, 13.5 ppm.

Viscosity

$$\eta(20\text{ }^{\circ}\text{C})=711\text{ cP}$$

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**Example 3: 1-n-Butyl-3-methylimidazolium lauryl sulfate ([BMIM]
[C₁₂H₂₅SO₄])**

30 Synthesis:

15.30 g (87.6 mmole) of 1-n-butyl-3-methylimidazolium chloride (BMIM Cl) and 26.60 g (minimum 87.6 mmole) of sodium lauryl sulfate (technical grade, content 95-99%) are dissolved in 50 ml of hot water. The water is slowly removed under vacuum. The solid formed is filtered off after adding methylene 35 chloride to the batch. The filtrate is washed with water until the aqueous phase is

colorless and free from chloride. The organic phase is dried over Na_2SO_4 . Concentrating and drying under a high vacuum gives 33.40 g of product (82.5 mmole; 94% of the theoretical yield, based on BMIM Cl) which is obtained as a white beige waxy solid.

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Melting point: 44 - 45 °C

NMR:

$^1\text{H-NMR}$ (300 MHz, CD_3CN): δ = 8.76 (s, 1H, N-CH-N), 7.43, 7.40 (two s, 1H in each case, N-CH₃), 4.17 (t, $J=7.3$ Hz, 2H, N-CH₂), 3.87 (s, 3H, N-CH₃), 3.83 (t, $J=6.6$ Hz, 2H, S-O-CH₂-), 1.84 (mult., 2H, N-CH₂-CH₂-), 1.58 (mult., 2H, S-O-CH₂-CH₂-), 1.40-1.25 (mult., 20H, S-O-CH₂-CH₂-(CH₂)₉-; N-CH₂-CH₂-CH₂-), 1.00-0.85 (t, each 3H, -CH₃) ppm.

$^{13}\text{C-NMR}$ (75 MHz, CD_3CN): δ = 136.2, 123.3, 121.9, 65.9, 48.9-48.7, 35.4, 31.3, 29.1-28.7, 25.5, 22.1, 18.6, 13.1, 12.4 ppm.

Hydrolysis tests

Example 4: Hydrolysis test with 1-n-butyl-3-methylimidazoliumoctyl sulfate ([BMIM] [$\text{C}_8\text{H}_{17}\text{SO}_4$])

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To 5 g of the ionic liquid of 1-n-butyl-3-methylimidazoliumoctyl sulfate ([BMIM] [$\text{C}_8\text{H}_{17}\text{SO}_4$]), 5 ml of water are added and heated to 80 °C. At intervals of 10 min, samples are taken from the reaction solution and pH measurements are carried out. The reaction solution is still pH-neutral after 2h at 80 °C which suggests that no hydrolytic decomposition of the ionic liquid takes place under these reaction conditions.

Comparative example 1: Hydrolysis test with 1-n-butyl-3-methylimidazolium methyl sulfate ([BMIM] [CH_3SO_4])

To 5 g of the ionic liquid of 1-n-butyl-3-methylimidazolium methyl sulfate ([BMIM] [CH_3SO_4]), 5 ml of water are added and heated to 80 °C. At intervals of 10 min, samples are taken from the reaction solution and pH measurements are carried out. The reaction solution exhibits a rapid decrease in the pH to 1 - 2 after the first measurement. This suggests that, under these reaction conditions, a hydrolytic decomposition of the ionic liquid takes place. Methanol and the acidic

hydrogen sulfate anion are liberated during this process.

Comparative example 2: Hydrolysis test with 1-ethyl-3-methylimidazoliummethyl sulfate ([EMIM] [C₂H₅SO₄])

5 To 5 g of the ionic liquid of 1-ethyl-3-methylimidazoliummethyl sulfate ([EMIM] [C₂H₅SO₄]), 5 ml of water are added and heated to 80 °C. At intervals of 10 min, samples are taken from the reaction solution and pH measurements are carried out. The reaction solution exhibits a rapid decrease in the pH to 1 – 2 after the first measurement. This suggests that, under these reaction conditions, a 10 hydrolytic decomposition of the ionic liquid takes place. Ethanol and the acidic hydrogen sulfate anion are liberated during this process.

Claims

The following is claimed

1. An ionic liquid with the general formula [cation] $[R' \text{-} \text{SO}_4]$ in which R' is a linear or branched, saturated or unsaturated, aliphatic or alicyclic alkyl group with 3 - 36 carbon atoms which is non-functionalized or functionalized with one or several X groups and X represents an $-\text{OH}$, $-\text{OR}''$, $-\text{COOH}$, $-\text{COOR}''$, $-\text{NH}_2$, $-\text{SO}_4$, $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$ or $-\text{CN}$ group, R'' being a branched or linear hydrocarbon chain with 1 - 12 carbon atoms.
2. The ionic liquid according to claim 2 characterized in that the [cation] used represents a

- quaternary ammonium cation with the general formula



- phosphonium cation with the general formula



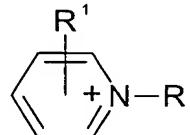
- imidazolium cation with the general formula



in which the imidazole core may be substituted with at least one group

selected from $\text{C}_1\text{-C}_6$ alkyl groups, $\text{C}_1\text{-C}_6$ alkoxy groups, $\text{C}_1\text{-C}_6$ aminoalkyl groups, $\text{C}_5\text{-C}_{12}$ aryl groups or $\text{C}_5\text{-C}_{12}\text{-aryl-C}_1\text{-C}_6$ alkyl groups,

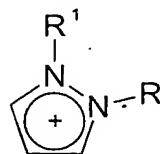
- pyridinium cations with the general formula



in which the pyridine core may be substituted with at least one group

selected from $\text{C}_1\text{-C}_6$ alkyl groups, $\text{C}_1\text{-C}_6$ alkoxy groups, $\text{C}_1\text{-C}_6$ aminoalkyl groups, $\text{C}_5\text{-C}_{12}$ aryl groups or $\text{C}_5\text{-C}_{12}\text{-aryl-C}_1\text{-C}_6$ alkyl groups,

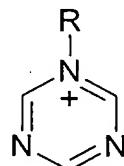
- pyrazolium cations with the general formula



in which the pyrazole core may be substituted with at least one group selected from C₁-C₆ alkyl groups, C₁-C₆ alkoxy groups, C₁-C₆ aminoalkyl groups, C₅-C₁₂ aryl groups or C₅-C₁₂-aryl-C₁-C₆ alkyl groups,

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- and triazolium cations with the general formula



in which the triazole core may be substituted with at least one group selected from C₁-C₆ alkyl groups, C₁-C₆ alkoxy groups, C₁-C₆ aminoalkyl groups, C₅-C₁₂ aryl groups or C₅-C₁₂-aryl-C₁-C₆ alkyl groups, and the radicals R1, R2, R3 are selected independently of each other from the group consisting of

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- hydrogen;
- linear or branched, saturated or unsaturated, aliphatic or alicyclic alkyl groups with 1 to 20 carbon atoms;

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- heteroaryl groups, heteroaryl-C₁-C₆ alkyl groups with 3 to 8 carbon atoms in the heteroaryl radical and at least one heteroatom selected from N, O and S, which may be substituted with at least one group selected from C₁-C₆ alkyl groups and/or halogen atoms;

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- aryl groups, aryl-C₁-C₆ alkyl groups with 5 to 12 carbon atoms in the aryl radical, which may optionally be substituted with at least one C₁-C₆ alkyl group and/or a halogen atom;

and the radical R is selected from

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- linear or branched, saturated or unsaturated, aliphatic or alicyclic alkyl groups with 1 to 20 carbon atoms;
- heteroaryl-C₁-C₆ alkyl groups with 3 to 8 carbon atoms in the aryl radical and at least one heteroatom selected from N, O and S, which may be substituted with at least one C₁-C₆ alkyl group and/or halogen atoms;

- aryl-C₁-C₆ alkyl groups with 5 to 12 carbon atoms in the aryl radical, which may optionally be substituted with at least one C₁-C₆ alkyl group and/or halogen atoms;

3. The ionic liquid according to claims 1 and 2 characterized in that the ionic liquid carries an anion with the empirical formula [C₄H₉SO₄].

5 4. The ionic liquid according to claims 1 and 2 characterized in that the ionic liquid carries an anion with the empirical formula [C₈H₁₇SO₄].

5 5. The ionic liquid according to claims 1 and 2 characterized in that the ionic liquid carries an anion with the empirical formula [C₁₂H₂₅SO₄].

10 6. A chemical reaction in which an ionic liquid defined by claims 1 – 5 is used as solvent, solvent additive or phase transfer catalyst.

7. The chemical reaction according to claim 6 characterized in that the reaction is a reaction catalyzed by a transition metal.

8. The chemical reaction according to claims 6 or 7 characterized in that the reaction belongs to a group of reactions comprising hydroformylation reactions, oligomerization reactions, esterifications, isomerization reactions and reactions for amide bond linkage.

15 9. The chemical reaction according to claim 6 characterized in that the reaction is a reaction catalyzed by an enzyme or by another biocatalyst.

20 10. The chemical reaction according to claims 6 and 9 characterized in that the reaction belongs to a group of reactions comprising oligomerization reactions and other C-C bond linkage reactions, esterifications, isomerization reactions and reactions for amide bond linkage.

11. A material separation process using, as solvent or solvent additive, an 25 ionic liquid defined by claims 1 - 5.

12. An apparatus for heat exchange in which an ionic liquid defined by claims 1 - 5 is used as heat carrier or heat carrier additive.

13. A use of an ionic liquid according to claims 1 - 5 as solvent.

14. The use of an ionic liquid according to claims 1 - 5 as solvent additive.

30 15. The use of an ionic liquid according to claims 1 - 5 as phase transfer catalyst.

16. The use of an ionic liquid according to claims 1 - 5 as solvent extraction agent.
17. The use of an ionic liquid according to claims 1 - 5 as heat carrier.